Original Article

Linear and crosslinked polyimide aerogels: synthesis and characterization

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\textbf{A B S T R A C T}

Linear and crosslinked polyimide aerogels have been synthesized by means of a simple and eco-friendly process. Water-soluble poly(amic acid), PAA, solution was produced and thermal imidization was employed. Furthermore, freeze drying was used. In the present work, the influence of the solid content of the PAA solution and the crosslinking addition on the properties of the resulted aerogels were evaluated. An increase in solid content resulted in denser structures. Thermogravimetric analysis demonstrated thermal stability of polyimide aerogels up to 550 °C. Moreover, the crosslinking addition resulted in mechanical properties improvements. In addition, the obtained polyimide aerogels retained an oil amount of 14 times higher than its dry weight. Besides, polyimide aerogels showed very good values of sound absorption coefficient (maximum value of 0.91) and low thermal conductivities (0.038–0.045 W/mK). Summarizing, PI aerogels presented very good thermal and acoustic insulation properties, excellent thermal stability and good oil sorption capability.

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1. Introduction

Aerogels are ultralight materials with high porosity, very low density, large surface area and low values of thermal conductivity. As a consequence of their interesting properties, they can be used in many fields like energy storage, environmental remediation, catalysis, sensor, cosmic dust collection and thermal and acoustic insulation [1–7].

Organic aerogels have attracted many attention as a consequence of their exceptional properties in comparison with inorganic aerogels. Organic aerogels present superior mechanical properties, easier availability and lower cost [8]. However, organic aerogels have low thermal and dimensional stability at high temperatures. Thus, they could not be used in applications that require high thermal stability such as thermal protecting coatings or interlayer electrically insulation systems for microelectronic device fabrication [9]. In this
In regard, the necessity of high temperature resistant organic aerogels is increasing.

Polyimide (PI) is a type of high performance polymer with high thermal stability and glass transition temperatures, good mechanical properties, low dielectric constant as well as outstanding chemical and radiation resistance. Polyimides are used in a great number of applications in aerospace, optoelectronic, microelectronic and electrical industries [10,11]. Therefore, polyimides in the form of aerogels are competitive materials with good comprehensive properties. Linear and crosslinked polyimide aerogels have been reported. Previously, linear polyimide aerogels were synthesized from dianhydrides and diamines in polar aprotic solvents with the poly(amic acid) formation. Contacting the poly(amic acid) in a first solvent with a dehydrating agent, the polyimide gel was formed by chemical imidization because the polyimide was insoluble and separated from the solvents. However, the polyimide aerogels required a thermal treatment (before or after supercritical drying) to convert the residual amic acid group to the imide group and to rearrange the isomide group produced during chemical imidization to the imide group. After the wet gel formation, it was required the supercritical drying to form the aerogel. On the other hand, other route to synthesize linear PI aerogels is based on supercritical drying of PI wet gels synthesized from a dianhydride and a diisocyanate instead of diamine without dehydrating agent addition [12]. Although the cost of the process to synthesize PI aerogels from dianhydride and a diisocyanate at relatively low temperatures is lower than that from dianhydride and diamine at high temperatures, the resulted aerogels presented inferior mechanical properties [13].

**Fig. 1 – General synthesis route for linear polyimide aerogels.**
On the other hand, there are many researches based on the synthesis of crosslinked polyimide aerogels such as crosslinking anhydride capped poly(amic acid) oligomers with aromatic triamines and thermally imidized [14,15]. PI aerogels synthesized by means of this route do not present a well-formed network as a consequence of the amic acid hydrolysis during thermal imidization that breaks up the network structure. Other researchers synthesized crosslinked polyimide aerogels by means of crosslinked poly(amic amid) structures, followed by chemical imidization at room temperature and supercritical drying [16-18]. However, crosslinked poly(amic acid) was not completely imidized by chemical imidization at room temperature and formed too quickly as a consequence of the chemical imidization reagents [19].

In this study, linear and crosslinked polyimide aerogels were synthesized by means of a simple and eco-friendly fabrication. Water-soluble poly(amic acid) (PAA) solution was produced to carry out the freeze-drying process. Furthermore, thermal imidization was employed, eliminating the need for chemical imidization reagents and the problem of incomplete imidization. Then, it was followed by freeze drying, avoiding expensive and time-consuming supercritical drying. Moreover, the properties of the synthesized aerogels were studied in order to analyze their behavior in several industrial applications.

2. Experimental

2.1. Materials

4,4′-Oxydianiline (ODA), 3,3′,4,4′-biphenyltetra carboxylic dianhydride (BPDA), 1-methyl-2-pyrrolidone (NMP), tris(4-aminophenyl amine) (TAPA) and triethylamine (TEA) were purchased from Sigma-Aldrich. Water was purified by distillation followed by deionization using ion-exchange resins. Reused cooking oil and motor oil were supplied by research labs from the University of Castilla-La Mancha.

2.2. Synthesis of polyimide aerogels (PI aerogels)

Since poly(amic acid), the precursor of polyimides, are soluble only in toxic polar solvents, careful handling is required to avoid environmental problems. Furthermore, poly(amic acid) presents storable problems due to its hydrolytic instability [20]. In this regard, water-soluble poly(amic acid) (PAA) solution, which is beneficial for both environmental and practical issues to carry out the freeze-drying process, was synthesized.
Thus, water-soluble poly(amic acid) (PAA) \cite{21,22} intermediate was generated from a polycondensation reaction (as shown in Figs. 1 and 2 for linear and crosslinked PI aerogels, respectively) between aromatic acid dianhydride (BPDA) and aromatic diamine (ODA) procedure in NMP under nitrogen atmosphere. For crosslinked polyimide aerogels, TAPA was incorporated (taking into account that the molar ratio of amino to anhydride equals to 1:1) to form TAPA–PAA intermediate. Then, the intermediate PAA (for linear PI aerogels) or TAPA–PAA (for crosslinked PI aerogels) was precipitated with deionized water and the precipitate was washed several times with water and dried under vacuum for further use.

A certain amount of TEA was first dissolved in deionized water, the solution was continually stirred in an ultrasound bath for 30 min. Subsequently, a certain amount varying between 1 and 5 wt.% of dried PAA or TAPA–PAA was added to the TEA–water solution and stirred for 3–5 h. Then, PAA or TAPA–PAA/TEA–water solution for linear or crosslinked PI aerogels, respectively, was introduced into the trays of the laboratory freeze-dryer, frozen for 6 h at −60 °C and, finally, sublimated under vacuum for 24 h. Later, dried samples were placed in a vacuum oven for 2 h at 200 °C to carry out the thermal imidization and PI aerogels were obtained (Figs. 1 and 3 for linear and crosslinked PI aerogels, respectively). Table 1 shows the synthesized samples and Fig. 4 shows the schematic process to obtain PI aerogels.

### 2.3. Characterization of nanoclay-based PVA aerogels

The morphological structure was analyzed using a scanning electron microscope (SEM) system (Model Phenom-ProX, Phenom World). To analyze the pore size distribution in detail, a mercury porosimeter (Quanbachore Foremaster) was used. The methodology is based on the physical penetration of mercury into the pores of the materials when a sufficient pressure is applied to allow it to intrude. The resulting mercury volume registration, as a function of increasing pressure, allows the generation of the pore size distribution \cite{23}. The bulk density was calculated from weight and physical dimension of samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of aerogel</th>
<th>Solid content of PAA solution (wt.%)</th>
<th>Crosslinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>P10.01</td>
<td>Linear</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>P10.03</td>
<td>Linear</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>P10.04</td>
<td>Linear</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>P10.05</td>
<td>Linear</td>
<td>5</td>
<td>–</td>
</tr>
<tr>
<td>PIC0.03</td>
<td>Crosslinked</td>
<td>3</td>
<td>TAPA</td>
</tr>
</tbody>
</table>

Table 1 – Polyimides aerogels denomination.

Contact angles were measured using an optical tensiometer (Theta Lite) supplied by BIOLIN Scientific at 25 °C. Two microliters of water were dropped onto the surface of polyimide aerogels. The average contact angle value was obtained by measuring it at three different positions in the sample.

Changes induced in the structure of the samples after imidization and crosslinking addition were studied using an infrared spectrometer (Spectrum Two, Perkin Elmer) in the range of 4000–5000 cm\(^{-1}\).

The Young's modulus was determined using dynamic mechanical analysis (DMA) 1STARE System (Mettler Toledo) by means of stress–strain analysis in compression mode. Furthermore, the glass transition temperature was identified by the peak temperature of the tan \(\delta\) versus temperature curves by means of thermomechanical analysis.

Thermal conductivity measurements were performed by using a Heat Flow Meter (LINOSEIS HFM 300) with a high level of accuracy. The instrument is designed per ASTM C518, JIS A1412, ISO 8301 and DIN 12667. The methodology is based on the heat flow measurements when a sample is located between a hot plate and a cold plate. It allows one to determine thermal conductivities in a wide range from 0.001 to 2.5 W/(m.K). Furthermore, it can operate at different temperatures (from −30 to 90 °C).

Thermogravimetric analysis (TGA) using a thermal analyzer (Mettler Toledo TGA/DSC 1 STARE System) was carried out to study the behavior of the synthesized aerogels with the temperature. Pyrolysis was carried out at a heating rate of 10 °C/min under nitrogen atmosphere using a gas flow of 100 NmL/min from room temperature to 1000 °C.

The acoustic characterization of the aerogels was carried out in a traditional impedance tube (Bruel & Kjaer) equipped with two microphone locations and a digital frequency analysis system for evaluating the sound absorption coefficient for normal sound incidence (ISO 10534-2) \cite{24}. Acoustic tests for each sample at the same and different positions inside the tube were repeated at least five times.

### 2.4. Oil sorption testing method and oil characterization

Oil sorption capability of polyimide aerogels was measured using a slightly modified method based on the ASTM Standard F726-06 test for the sorbent performance. First, aerogel sample (20 mm (long) × 20 mm (high) × 10 mm (wide)) was weighed and introduced in 600 mL of oil for a certain time. Then, the wet sample was removed in a vertical orientation from the liquid using a stainless-steel mesh basket and drained for a certain time. After that, the sample was weighed again. Each test was
repeated several times. Short test was carried out by aerogel immersion in oil for 15 min and drained for other 2 min and, then was weighted.

The oil sorption capability was calculated as shown in Eq. (1):

\[
\text{Oil sorption capability (}\text{q}\text{)} = \frac{S_n - S_0}{S_0} = \frac{S_n}{S_0}
\]

where \(S_0\) is the initial dry sorbent weight, \(S_n\) is the weight of sorbent with oil at the end of the sorption test and \(S_n\) is the net oil sorbed. All weights were measured in grams.

The oil viscosity at 40 °C was measured using a viscometer (Tamson TV2000) by Labovico B.V. The oil density was measured at 15 °C using a digital density meter (DMA™ 5000M) supplied by Anton Paar.

3. **Results**

In this study, linear and crosslinked polyimide aerogels (PI aerogels) were synthesized. Furthermore, linear aerogels with solid content of PAA solution varying between 1 and 5 wt.% were synthesized as well as crosslinked polyimide aerogels with 3 wt.% of solid content of PAA solution. It is necessary the creation of water-soluble poly(amic acid), PAA, solution due to water is the most of the pore forming agent of freeze-drying. Figs. 1 and 2 show synthesis routes for linear and crosslinked PI aerogels, respectively. First, PAA intermediate was generated from the reaction of ODA and BPDA. Then, for crosslinked polyimide aerogels, TAPA was incorporated to form TAPA–PAA. Finally, poly(amic acid) solution was prepared by dissolving PAA or TAPA–PAA in an aqueous solution of TEA. After freeze-drying, the samples were heated under vacuum to carry out the thermal imidization to synthesize linear and crosslinked PI aerogels, Figs. 1 and 3, respectively. Finally, PI aerogels were analyzed by means of different characterization techniques.

3.1. **Linear polyimide aerogels**

3.1.1. **Morphology and structure of polyimide aerogels** Fig. 5 shows a picture of sample before (PAA sample) and after imidization (PI sample) with 3 wt.% of solid content of PAA solution. The aerogels modified from white to dark yellow in appearance. Fourier-transform infrared spectroscopy analysis (FTIR) of PAA and PI samples is presented in Fig. 6a. For PAA (sample before imidization), the characteristic absorption peak at 1660 cm\(^{-1}\) is assigned to the stretching vibrations of C=O and 1535 cm\(^{-1}\) associated to amide C–N. However, for the aerogels after imidization, FTIR spectrum is dominated by the imide ring at 1775 cm\(^{-1}\) attributed to the asymmetrical carbonyl stretching vibration and 1720 cm\(^{-1}\) to the symmetrical...
carbonyl stretching vibrations. A band at around 1860 cm\(^{-1}\), which would indicate the existence of unreacted anhydride, was not observed. Furthermore, the peak around 1370 cm\(^{-1}\) is attributed to C–N bond stretching and the peaks 1050 and 723 cm\(^{-1}\) corresponded to imide ring deformation \([18,21,25]\). Therefore, FTIR measurements prove the successful amidation of PAA to PI.

The morphologies of the linear polyimides aerogels were studied by SEM (Fig. 7a–c). The SEM images clearly showed many layers tangled together, which corresponds with typical morphology of polymeric aerogels \([26]\). Furthermore, as shown, the distribution of the nanofibers has many pores among them. The density and pore size of polyimide aerogels can be adjusted through the solid content of the PAA solution. As expected, Fig. 7a–c shows that an increase in solid content resulted in denser fibrillar structures with smaller pore size \([10]\). Thus, the bulk density of the polyimide aerogels increased with solid content of PAA solution increase (Fig. 8). These findings were in good agreement with pore size distribution (PSD) curves shown in Fig. 9. It can clearly be seen that the solid content had a significant effect on the porosity of the resulting aerogels. The peak of the PSD profiles shifted to higher pore size with solid content reduction.

The contact angle of linear PI aerogels was 95° as shown in Fig. 10. Furthermore, droplets could attach to the aerogels and exhibited a petal effect that prohibited the rolling off the water.
Fig. 7 – SEM images of: (a) PI0.01; (b) PI0.03; (c) PI0.05 and (d) PIC0.03.

Fig. 8 – Bulk density of samples synthesized with different amount of solid content of PAA solution.

Fig. 9 – Pore size distribution of linear aerogels synthesized with different amount of solid content of PAA solution.

Furthermore, the oil sorption capabilities of the polyimide aerogels were investigated as there are few researches based on this application. To investigate the oil sorption behavior associated to the polyimide aerogels, cooking oil was tested.
The cooking oil used to carry out this study had 0.058 Pa s of viscosity at 40 °C and 0.933 g/cm³ of density at 15 °C. It was found that after oil dropping over the aerogels surface, the oil droplet immediately spread on their surface with an oil contact angle of 0°, which indicated that all samples were superoleophilic. After short sorption test, the oil sorption capability of PI0.03 resulted in 14 g oil/g aerogel. These results demonstrate that polyimide aerogels have good sorbent properties allowing to retain an amount of oil 14 times higher than its dry weight. These PI aerogels are very competitive as sorbent materials in comparison with other PI aerogels that can only retain an amount of oil equal to its dry weight [29].

3.1.2. Thermal properties of polyimide aerogels
Thermal stability of the samples was tested by TGA analysis in nitrogen atmosphere. Fig. 11 shows the pyrolysis process for sample synthesized using 3 wt.% of solid content of PAA solution, before (PAA) and after (PI) imidization. PAA0.03 sample exhibited three decomposition stages. The first stage, which occurred in the range 25–215 °C, corresponds to the evaporation of residual solvents such as NMP and adsorbed water. The second stage, which ranged from 215 to 290 °C can be assigned to the continuous weight loss of 10% of the oligomer due to imidization of PAA [30]. Then, the weight became almost constant and the last decomposition stage (550–600 °C) indicated a maximum weight loss of approximately 16% due to the thermolysis of PI. At the end of this stage, around 35 wt % of PAA remained at 1000 °C.

The TGA curve of PI0.03 sample exhibited good thermal stability up to 550 °C. The small variations of weight loss around 300 °C could be due to the existence of residual NMP solvent [31]. The significant mass losses at 550 °C were caused by the thermal decomposition process of the main chains of PI molecule [32]. About 50 wt.% of PI aerogel remained at 1000 °C, similar to that reported in other works [33]. The high residual weight percentage at 1000 °C of PI0.03 sample was ascribed to their high aromatic content [34].

The glass transition temperature (Tg) of PI aerogels was identified by the peak temperature of the tan δ versus temperature curves. After several measurements of PI0.03 sample, the Tg is ∼280 °C, similar to that reported in other works [19].

Moreover, a thermal conductivity analysis was also studied to determine the thermal insulation behavior of the synthesized aerogels resulting in values of thermal conductivity in the range of 0.038–0.045 ± 0.006 W/m K. These results demonstrated that PI aerogels could be used in the building insulation industry.

3.1.3. Acoustic properties of polyimide aerogels
Sound absorption coefficient, ratio of the absorbed energy by a material to the incident energy, was measured for PI0.03 sample to study the possibility of using polyimide aerogels with enhanced acoustic properties. Sound absorption coefficient varies between 0 and 1. The higher the value of this ratio, the better the absorption is. The measurements were carried out in a frequency interval from 1600 to 6400 Hz and were repeated at least five times for each position of the sample. Fig. 12 shows the frequency-dependence of sound absorption coefficients for PI0.03 sample with 0.5 cm of thickness when it was exposed to incident sound waves. It is well known that the material thickness plays an important part in the capacity for sound absorption of materials at low frequencies. The reason is that lower frequencies, waves have higher wavelength, which means the thicker materials contributed in better sound absorption. Thus, the sound absorption coefficient of PI0.03 sample was low at low frequencies. Furthermore, the morphology of the pores in porous materials has an important influence on the sound absorption coefficient. Porous materials have cavities, channels or interstices so that sound waves are able to enter through them [34–36]. Closed pores are isolated from their neighbors and are less efficient than open pores in absorbing sound energy. However, open pores have continuous channels of communication with the external surface and have a great influence on the sound absorption [34–36]. Results showed a better acoustic behavior of the top face of the sample,
probably as consequence of the morphology of its pores, with a maximum sound absorption coefficient of 0.91.

3.2. Crosslinked polyimide aerogels

Fourier transform infrared (FTIR) spectra of crosslinked PI aerogels (PIC aerogels), as seen in Fig. 6b, contains the same characteristic peaks of linear PI aerogels. The spectrum contained the main characteristics peaks of polyimide. Furthermore, as commented for linear PI aerogels, bands at 1660 cm\(^{-1}\) (C=O) and 1535 cm\(^{-1}\) (amide C−N) were absent further indicating that imidization was complete. Moreover, the FTIR spectrum of crosslinked PI aerogels presented a band around 1280 cm\(^{-1}\) attributed to aromatic amine from TAPA.

Fig. 7d shows SEM micrograph of crosslinked PI aerogels synthesized using 3 wt.% of solid content of PAA solution. As shown, the crosslinking introduction, resulted in a three-dimensional network of polyimide fibers tangled together as reported in other works [10,18].

Furthermore, the stress–strain analysis for the linear and crosslinked PI aerogels were carried out. The elastic modulus (or Young's modulus) was determined from the slope of the linear part of the stress–strain curve, where an elastic behavior of the aerogels was observed. It has been considered a strain range from 0 to 0.07 because it was the region with an elastic behavior. After the measurements, the Young's modulus improved in 34% with the crosslinking agent addition.

On the other hand, the glass transition temperature (\(T_g\)) of crosslinked PI aerogels was evaluated to study the effect of the structure on the \(T_g\) of the polymer. After several measurements of PIC0.03 sample, the \(T_g\) was approximately 290 °C, higher than PI0.03 sample. This fact could be due to the presence of aromatic structures of TAPA that complicate the chain rotation and increases the intermolecular cohesive forces. Thus, it can be corroborated that the presence of crosslinking agent increases the \(T_g\) as reported in other works [37]. Finally, the thermal conductivity of PIC0.03 sample was carried out in order to evaluate its behavior as building insulation material, resulting in 0.040 W/m K.

Summarizing, PI aerogels present excellent thermal stability and good thermal and acoustic insulation properties. Furthermore, they can be used as sorbent materials with high sorption capability.

4. Conclusions

Linear and crosslinked polyimide aerogels have been synthesized by means of a simple and eco-friendly process and thermally imidized. Fourier-transform infrared spectroscopy analysis demonstrated the successful thermal imidization. Furthermore, an increase in solid content resulted in denser fibrillar structures with smaller pore size. On the other hand, the thermogravimetric analysis demonstrated the high thermal stability of polyimide aerogels up to 550 °C. On the other hand, crosslinked PI aerogels presented better mechanical properties (Young’s modulus increase in 34%) and higher glass transition temperature than linear PI aerogels. In addition, the synthesized polyimide aerogels were evaluated as sorbent materials for oil spill, resulting in a retained oil amount of 14
times higher than its dry weight. Furthermore, polyimide aerogels were analyzed as possible acoustic and thermal insulation materials. Results showed very good values of sound absorption coefficient (maximum value of 0.91 at high frequencies) and thermal conductivities (0.038–0.045 ± 0.006 W/m K). Summarizing, PI aerogels present very good thermal and acoustic insulation properties, excellent thermal stability and good oil sorption capability.

**Conflicts of interest**

The authors declare no conflicts of interest.

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